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Thermodynamics of Micellar Systems

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Published in:
Advances in Colloid and Interface Science

DOI:
[10.1016/0001-8686\(95\)00252-L](https://doi.org/10.1016/0001-8686(95)00252-L)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1995

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Blandamer, M. J., Cullis, P. M., Soldi, L. G., Engberts, J. B. F. N., Kacperska, A., & Os, N. M. V. (1995). Thermodynamics of Micellar Systems: Comparison of Mass Action and Phase Equilibrium Models for the Calculation of Standard Gibbs Energies of Micelle Formation. *Advances in Colloid and Interface Science*, 58(2-3), 171-209. [https://doi.org/10.1016/0001-8686\(95\)00252-L](https://doi.org/10.1016/0001-8686(95)00252-L)

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THERMODYNAMICS OF MICELLAR SYSTEMS: COMPARISON OF MASS ACTION AND PHASE EQUILIBRIUM MODELS FOR THE CALCULATION OF STANDARD GIBBS ENERGIES OF MICELLE FORMATION

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LIST OF SYMBOLS

aq	aqueous solution
c_r	reference concentration 1 mol dm^{-3}
c_j	concentration of substance j
cmc	critical micellar concentration
cmm	critical micellar molality
cmx	critical micellar mole fraction
e	charge of proton
eq	equilibrium
f	activity coefficient
f_1	(rational) activity coefficient of substance 1
f_j	(rational) activity coefficient of solute j
f_j^*	asymmetric activity coefficient of solute j
G	Gibbs energy
H	enthalpy
l	liquid
M_1	molar mass of substance 1
m_j	molality of solute j
mix	liquid mixture
n_1	amount of substance 1
n_j	amount of substance j
p	pressure
p^0	standard pressure, 10^5 N m^{-2}
Q	stoichiometric parameter for a salt
R	gas constant; $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
S	entropy
T	temperature
m_j	molality of solute j
m^0	1 mol kg^{-1}
N	aggregation number for micelles
V	volume
x	mole fraction
x_1	mole fraction of solvent; water
z_i	charge number for ion i
$\Delta_{\text{mic}} G^0$	standard Gibbs energy for the formation of one mole of micelles from N moles of monomer
$\Delta_{\text{mic}} G^0(N)$	standard Gibbs energy for the formation of micelles from one mole of monomer

β	measure of counterion binding by micelles
ϕ	practical osmotic coefficient
γ_j	activity coefficient for neutral solute j , molality scale
γ_{\pm}	mean ionic activity coefficient for a salt in solution, molality scale
μ	chemical potential
$\mu_1^0(\ell;T)$	standard chemical potential of substance 1
$\mu_j^0(\ell;T)$	standard chemical potential of substance j
ν	stoichiometry of salt in solution; $= \nu_+ + \nu_-$
ν_+	number of moles of cations produced on complete dissociation by one mole of salt
ν_-	number of moles of anions produced on complete dissociation by one mole of salt
*	pure substance

ABSTRACT

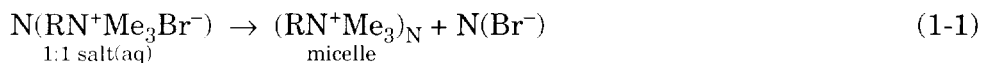
Micellar colloids are distinguished from other colloids by their association–dissociation equilibrium in solution between monomers, counter-ions and micelles. According to classical thermodynamics, the standard Gibbs energy of formation of micelles at fixed temperature and pressure can be related to the critical micelle concentration. This relation is different for two models which are widely used to describe micelle formation, namely the Phase Separation and the Mass Action Models. These approaches and the assumptions upon which they are based are analysed in this paper. We show that the two models can be generalised to include surfactant salts having different stoichiometries.

1. INTRODUCTION

The term amphipathic in the context of aqueous solutions means that a given solute has dual characteristics [1]. Here we are particularly concerned with ionic surfactants having, for example, the general formulae $\text{CH}_3(\text{CH}_2)_n\text{NMe}_3^+\text{Br}^-$ and $\text{CH}_3(\text{CH}_2)_n\text{SO}_3^-\text{Na}^+$. The thermodynamic (together with transport and spectroscopic) properties of aqueous solutions containing this class of solutes, surfactants, often undergo a dramatic change at some (low) critical concentration called the critical micellar concentration (composition), cmc [2,3]. These concentrations have been documented for a wide range of surfactants [4,5]. Below this concentration a given ionic surfactant usually exists as a strong electrolyte. At the cmc, the solute ions cluster to form micelles. Here we are

concerned with the properties of these solutions having compositions close to a cmc. We do not concern ourselves with post-micellar clusters formed at higher surfactant concentrations [6,7].

Although a quoted cmc often depends on the method used in its determination, the challenge is to use a measured cmc and other thermodynamic properties of the solutions and thereby obtain thermodynamic parameters which describe the formation of micelles from simple solutes. In the case of, for example, hexadecyltrimethylammonium bromide (CTAB) we write this process using the following equation:



In principle it is possible to describe this process using thermodynamic variables characterising the standard states for the salt and the micelles in a liquid system. Then $\Delta_{\text{mic}}G^0$ is the standard Gibbs energy of micelle formation from N moles of simple salt, $\text{RN}^+\text{Me}_3\text{Br}^-$. The definition together with the sign and magnitude of $\Delta_{\text{mic}}G^0$ is directly associated with the definitions of standard states for both the simple salt in solution and the micelles. The matter of these definitions is not a trivial issue as has been shown in another context [8]. Granted that $\Delta_{\text{mic}}G^0$ has been defined, this quantity can be reformulated in terms of an equilibrium constant describing micelle formation; Eq. (1-2).

$$\Delta_{\text{mic}}G^0 = -R \cdot T \cdot \ln K \quad (1-2)$$

In the discussion presented here we assume that all closed systems at fixed temperature and at fixed pressure are at a minimum in Gibbs energy when at thermodynamic equilibrium. In the latter state, the affinity for spontaneous change and the rate of change are zero [9]. Each system has a unique state where the Gibbs energy is a minimum [10]. We also assume that the systems described below are at ambient pressure which, for our purpose, is effectively the standard pressure, p^0 . Our approach is based on classical equilibrium thermodynamics. In other words, we do not consider mechanisms of micelle formation or deaggregation.

2. MICELLAR EQUILIBRIA

When small amounts of an amphiphilic substance such as CTAB are added to water there is no immediate signal from the properties of a

solution having a concentration below the cmc that macroions or aggregates can be formed. These new substances appear at a critical concentration. This almost catastrophic change in the nature of solutes in solution seems different in character from changes in chemical composition conventionally described in terms of chemical equilibria. Nevertheless, a convenient description of the system at the point where macroions/aggregates first appear is in terms of chemical equilibria. The assumption is made that in the closed system both micelles and monomers co-exist.

In the description adopted here, micelle formation is a one-step process [11] although as Desnoyers and coworkers [12] note the cmc has meaning only in relation to the model used to treat a set of data. If we represent a typical electrolyte (cf. CTAB) as the salt AM^+Br^- , the chemical equilibrium discussed above can be written in the following form.



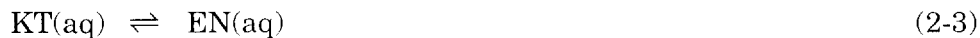
Then at equilibrium the chemical potentials of substances across the equilibrium sign are equal.

$$\text{N} \cdot \mu^{\text{eq}}(\text{AM}^+\text{Br}^-; \text{aq}; \text{at cmc}) = \mu^{\text{eq}}\{(\text{AM}^+\text{Br}^-)_{\text{N}}; \text{micelle at the cmc}\} \quad (2-2)$$

This equation forms the basis of the treatments discussed here. Equation (2-2) is the key thermodynamic condition. From this point, treatments diverge because they relate the two chemical potentials to the composition of the system in different ways. Therefore, we examine possible descriptions and explore their impact on a calculated $\Delta_{\text{mic}}G^0$.

In particular, we examine two commonly quoted models for micellar systems; (i) the Phase Equilibrium (PE) model and (ii) the Mass Action (MA) model. To set these treatments in context, we consider two simpler and possibly more familiar systems. In developing the argument, we imagine a flask containing n_1 moles of water (liquid) at fixed temperature and pressure. We further imagine that a small delivery tube allows n_x^0 moles of substance X (with $n_1 \gg n_x$) to be added repeatedly to the flask.

In the first example, substance X is propanone. A chemical equilibrium is rapidly established according to the following equation wherein both the keto-form, $\text{KT}(\text{aq})$ and the enol-form $\text{EN}(\text{aq})$ of propanone are *solutes* in aqueous solution.



At equilibrium, $\alpha \cdot n_x^0$ moles of added propanone are in the EN-form and $(1 - \alpha) \cdot n_x^0$ moles are in the KT-form where α is the degree of reaction. The equilibrium condition is re-expressed in Eq. (2-4) by an equality of (intensive) equilibrium chemical potentials (at fixed T and p).

$$\mu^{\text{eq}}(\text{KT}; \text{aq}; [(1 - \alpha) \cdot n_x^0]) = \mu^{\text{eq}}(\text{EN}; \text{aq}; [\alpha \cdot n_x^0]) \quad (2-4)$$

In terms of the models discussed below, the above is an MA description of an aqueous solution containing propanone. When a second aliquot of n_x^0 moles of propanone is added to the flask, the concentrations of *both* $\text{KT}(\text{aq})$ and $\text{EN}(\text{aq})$ increase. The newly added n_x^0 moles of propanone distribute between the EN and KT forms in order to hold the Gibbs energy of the system at a minimum and the chemical potentials of the two forms equal (Eq. (2-3)). The latter equality holds for k-injections such that at each stage the total amount of propanone in the system equals $k \cdot n_x^0$.

In the second example, substance X is (solid) silver chloride. If n_x^0 is small then after the first injection the silver chloride dissolves to form $\text{Ag}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$ in a single phase, an aqueous solution. Following further addition of $\text{AgCl}(\text{s})$ aliquots, $n^0(\text{AgCl})$, a solubility limit is reached described by a solubility product K_s which is characteristic of solvent T, p and $\text{AgCl}(\text{s})$. This dramatic change is signalled by the presence of two phases, solid and solution in the system. In the system containing $k \cdot n^0(\text{AgCl})$ where the concentration of $\text{AgCl}(\text{aq})$ is infinitesimally smaller than the solubility, all solute is in the form $\text{Ag}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$. With continued addition of $\text{AgCl}(\text{s})$, the concentrations of $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ remain constant. All that happens is that the amount of $\text{AgCl}(\text{s})$ in the system increases with each new addition of $n^0(\text{AgCl})$. In these solutions an equilibrium is established.



Then in terms of chemical potentials (at fixed T and p)

$$\mu^{\text{eq}}(\text{AgCl}; \text{s}) = \mu(\text{Ag}^+\text{Cl}^-; \text{aq}; [\text{solubility}])^{\text{eq}} \quad (2-6)$$

In terms of the models for micellar systems discussed below, the above treatment of the AgCl system uses a PE model in that the added substance X (here, AgCl) is present in two phases, solid and aqueous solution.

A clear distinction emerges between the MA model for propanone (aq) and the PE model for AgCl(aq). However, for surfactant systems, the distinction between the models becomes less striking than might be imagined, particularly as the aggregation number of the surfactant increases [13]. This important point is illustrated by considering an apolar solute in aqueous solution, X(aq) which forms an aggregate $X_N(\text{aq})$. Using the MA model, the chemical equilibrium between monomer, X(aq), and micelle, $X_N(\text{aq})$, can be written in the following form.



If the solution prepared using n_x^0 moles of substance X, at equilibrium there are ξ moles of aggregate and $(n_x^0 - N \cdot \xi)$ moles of monomer. At fixed temperature and pressure, an equilibrium constant K describes the chemical equilibrium. Then

$$\xi = K \cdot (n_x^0 - N \cdot \xi)^N \quad (2-8)$$

where for the neutral solute X(aq) (see below),

$$\Delta_{\text{mic}} G^0 = -R \cdot T \cdot \ln K = R \cdot T \cdot \ln (\text{cmc}) \quad (2-9)$$

To illustrate the argument we set $\text{cmc} = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ and calculate ξ as n_x^0 increases from zero to $15 \times 10^{-3} \text{ mol dm}^{-3}$ in a solution having volume 1.0 dm^3 . In Fig. 1, we show the dependence on n_x^0 of the amounts of monomer and micelle in solution for several cases characterised by the aggregation number N . In a computer program, n_x^0 was gradually increased. At and above the cmc, the program was used to calculate ξ as defined in Eq. (2-8) and hence to yield both $[X(\text{aq})]$ and $N \cdot [X_N(\text{aq})]$ above the cmc. The latter quantity refers to the amount of monomer X present as micelle. The plots describing the system where $N = 100$ are particularly interesting. Beyond the cmc and with increase in n_x^0 the amount of monomer according to this MA model stays almost constant (cf. Ag^+Cl^- (aq) as discussed above and the PE model). At the same time, the amount of aggregate in the system increases; cf. AgCl(s) in the discussion of the PE model described above. Thus according to the MA model where N is large, the concentration of monomer hardly alters as n_x^0 increases. Therefore if we can measure the cmc at a concentration of surfactant above the cmc, we can be reasonably confident that for large N , we can obtain $\Delta_{\text{mic}} G^0$

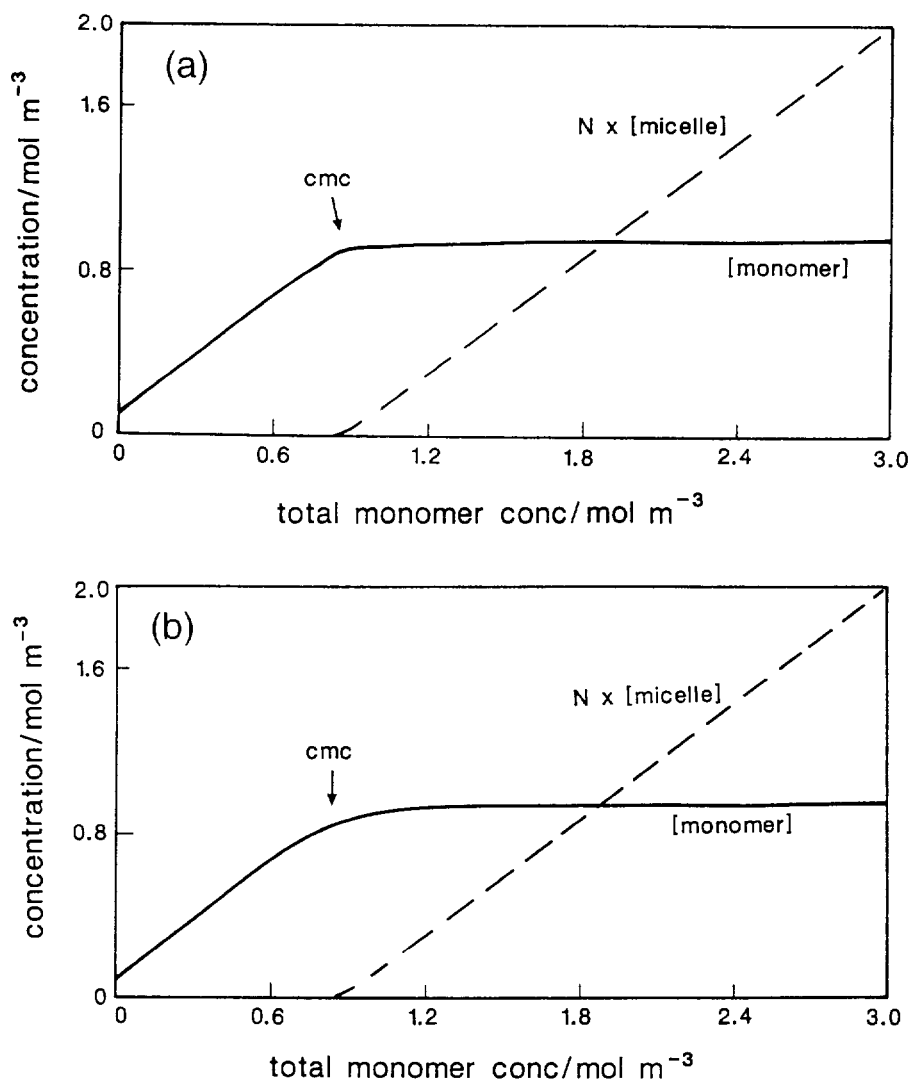


Fig. 1. Dependence of concentrations of micelles and of monomers as a function of total monomer concentration for four systems where the aggregation numbers are (a) 100, (b) 50, (c) 20 and (d) 2.

using Eq. (2-9). The major point to emerge is the similarity in composition profiles for the PE and MA models. Of course if this was not the case experiment would readily distinguish between the two models. The result is the controversy and strong statements claiming that either the PE or MA models cannot be allowed (e.g. Ref. [3], page 82). We address this

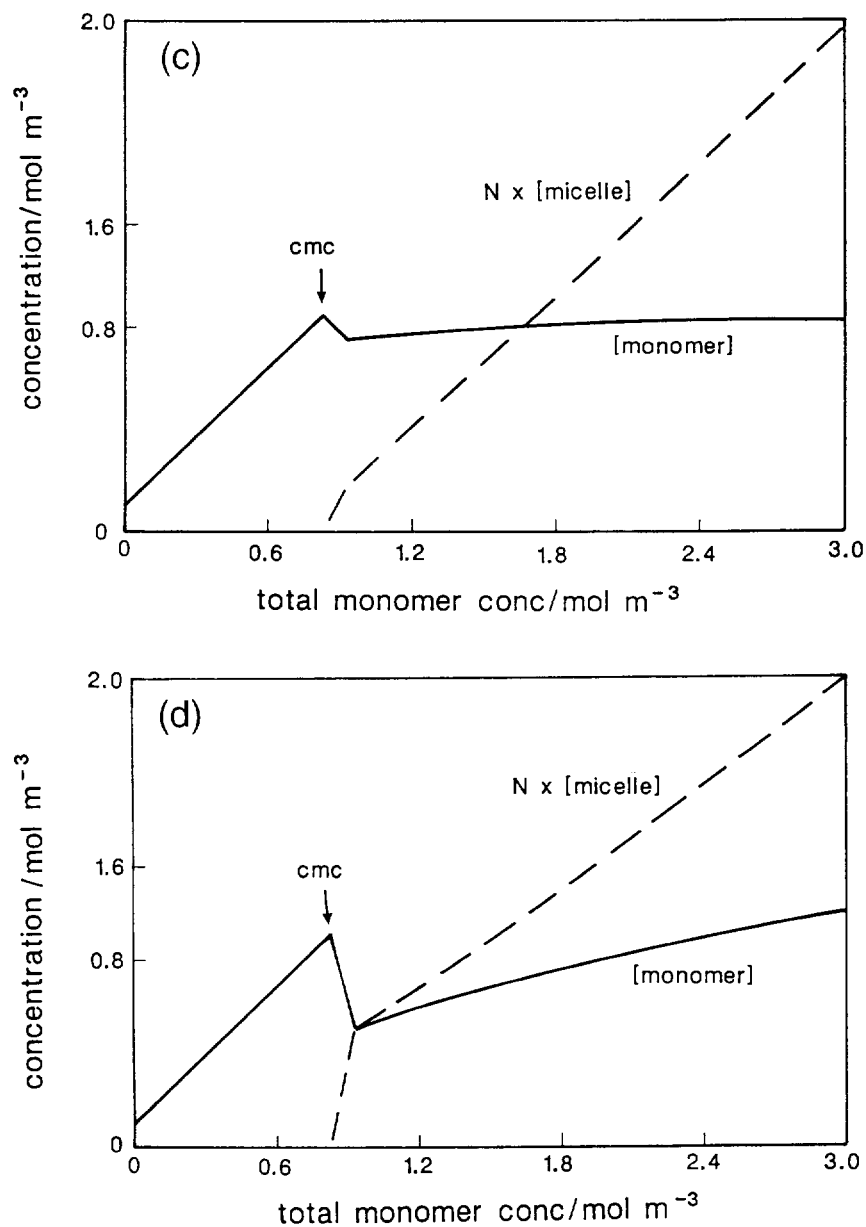


Fig. 1. (c) and (d). Caption opposite.

controversy in the following sections. We should point out that the analysis of trends in composition is slightly more complicated [14] in those cases where the surfactant is ionic but the underlying argument does not conflict with the points made above.

3. CHEMICAL POTENTIALS: LIQUID MIXTURES

We consider a liquid system prepared using n_1 moles of water and n_j moles of liquid substance j . The standard states for both substances are the corresponding pure liquid substances. The standard state chemical potentials are $\mu_1^0(\ell; T)$ and $\mu_j^0(\ell; T)$. For the liquid mixture, the mole fractions x_1 and x_j are given by $x_1 = n_1/(n_1 + n_j)$ and by $x_j = n_j/(n_1 + n_j)$. The chemical potentials of the two components in the liquid mixture are given by Eqs. (3-1) and (3-2).

$$\mu_1(\text{mix}; T) = \mu_1^*(\ell; T) + R \cdot T \cdot \ln(x_1 \cdot f_1) \quad (3-1)$$

where, by definition, limit $(x_1 \rightarrow 1)f_1 = 1.0$ at all T and p . Also,

$$\mu_j(\text{mix}; T) = \mu_j^*(\ell; T) + R \cdot T \cdot \ln(x_j \cdot f_j) \quad (3-4)$$

Again by definition, limit $(x_j \rightarrow 1)f_j = 1.0$ at all T and p ; f_j is the rational activity coefficient for substance j in the mixture. As the composition of the mixture approaches pure liquid j , f_j tends to unity. At the other end of the composition scale, f_1 approaches unity as the composition of the liquid mixture approaches pure water. The symbol $*$ highlights the fact that these chemical potentials refer to pure substances. These well-established equations are set down here in order to make a point. Although in the limit x_j tends to unity, f_j approaches unity, this rational activity coefficient can be significantly different from unity at the other extreme of the composition scale. An example [15] makes the point using tabulated data for water and tetrahydrofuran (THF) in a water + THF binary liquid mixture at 298.2 K. For the mixture where x_j is low ($j \equiv \text{THF}$ here), $x_j = 0.012$, $f_j = 16.39$ and $f_1 = 1.003$. For the mixture where $x_j = 0.92$, $f_j = 1.025$ and $f_1 = 5.925$. Therefore, in terms of the description of this system as a mixture of 'liquid water + liquid j ', we cannot, particularly for the water-rich systems, predict *a priori* the magnitude of f_j (i.e. the extent to which f_j is greater or less than unity although it is necessarily positive) and hence the extent to which $\mu_j(\text{mix}; T)$ differs from $[\mu_j^*(\ell; T) + R \cdot T \cdot \ln(x_j)]$, the ideal part of the chemical potential.

4. CHEMICAL POTENTIALS: AQUEOUS SOLUTIONS

We continue our description of a liquid formed by adding n_j moles of substance j to n_1 moles of water. In addition to using the mole fraction scale (Eq. (3-1)), we shift our description to that of a solution, volume V ,

of solute j in the solvent water, molar mass M_1 . The molality, $m_j = n_j/(n_1 \cdot M_1)$ and concentration $c_j = n_j/V$. In the aqueous system the chemical potentials of water and substance j are $\mu_1(\text{aq}; T)$ and $\mu_j(\text{aq}; T)$. But of course we could have used the same symbols as we used in the previous section; $\mu_j(\text{mix}; T) \equiv \mu_j(\text{aq}; T)$ and $\mu_1(\text{mix}; T) \equiv \mu_1(\text{aq}; T)$. The point is that the thermodynamic state variables and partial molar properties such as chemical potentials are not dependent on our description of a given system. This point is carefully developed by Hammett [16].

5. CHEMICAL POTENTIALS: AQUEOUS SOLUTIONS; MOLE FRACTION SCALE

If we describe a liquid system as an aqueous solution of solute j , we have several methods for relating $\mu_j(\text{aq}; T)$ and the composition. On the mole fraction scale we use Eq. (5-1).

$$\mu_j(\text{aq}; T) = \mu_j^0(\text{aq}; T; \text{x-scale}) + R \cdot T \cdot \ln(x_j \cdot f_j^*) \quad (5-1)$$

Here f_j^* is the asymmetric activity coefficient such that, by definition, $\lim_{x_j \rightarrow 0} f_j^* = 1.0$ at all T and p . In other words, the properties of solute j approach ideal as the mole fraction of solute j tends to zero; $\mu_j^0(\text{aq}; T; \text{x-scale})$ is the chemical potential of solute j in an ideal ($f_j^* = 1.0$) aqueous solution at the same temperature where the mole fraction of solute is unity. The reference state is the hypothetical solution where x_j and f_j^* are unity at the same T and p . In the context of the discussion below, we note that in switching descriptions of the system from mixture to solution, we switched f_j and $\mu_j^*(\ell; T)$ consistently to f_j^* and $\mu_j^0(\text{aq}; T; \text{x-scale})$ respectively. In dilute solutions containing solute j , f_j^* is likely to be close to unity but, as commented above, the rational activity coefficient f_j is likely to be very different from unity. The latter point is important in the context of how a given system is described.

Suppose a system is prepared by mixing n_1 moles of water and n_j moles of substance j . The composition is expressed in terms of mole fraction x_j but two descriptions are used.

Liquid mixture (cf. Eq. (3-2))

$$\mu_j(\text{system}; T) = \mu_j^*(\ell; T) + R \cdot T \cdot \ln(x_j \cdot f_j) \quad (5-2)$$

Solution (cf. Eq. (5-1))

$$\mu_j(\text{system}; T) = \mu_j^0(\text{aq}; T; \text{x-scale}) + R \cdot T \cdot \ln(x_j \cdot f_j^*) \quad (5-3)$$

Hence,

$$\mu_j^0(\text{aq}; T; \text{x-scale}) - \mu_j^*(\ell; T) = R \cdot T \cdot \ln(f_j/f_j^*) \quad (5-4)$$

The ratio of the activity coefficients, f_j/f_j^* , is related to the difference in chemical potentials of substance j in the two states. In fact, the difference, $\mu_j^0(\text{aq}; T; \text{x-scale}) - \mu_j^*(\ell; T)$, is conventionally described as a transfer parameter, being an important quantity in discussions of the solubilities of compounds in, for example, aqueous solutions.

If the claim is made that the properties of substance j in the system are ideal for both descriptions, f_j must equal f_j^* , both being unity. This is unlikely to be the case. We return to this point below when we compare models for micellar systems.

6. CHEMICAL POTENTIALS: AQUEOUS SOLUTIONS; MOLALITY SCALE

In an analysis of the properties of a solute in dilute aqueous solutions the molality scale is often preferred to the mole fraction scale on arithmetic grounds. On the mole fraction scale the difference in composition between two solutions is only apparent in the third or fourth significant figure between 0.0 and 0.1 with respect to the solute.

The chemical potential of solvent water in an aqueous solution at fixed T and fixed pressure is related to the molality using Eq. (6-1).

$$\mu_1(\text{aq}) = \mu_1^*(\ell) - \phi \cdot R \cdot T \cdot M_1 \cdot m_j \quad (6-1)$$

For an ideal aqueous solution, the practical osmotic coefficient ϕ is unity at all T and p . For an ideal solution $\mu_1(\text{aq}) < \mu_1^*(\ell)$; added solute stabilises the solvent. As the system becomes more dilute (i.e. m_j decreases) so the chemical potential of the solvent in solution approaches that of the pure liquid solvent.

Turning to the solute, the chemical potential of solute j in an aqueous solution is related to molality m_j using Eq. (6-2) which incorporates a solute activity coefficient γ_j .

At temperature T ,

$$\mu_j(\text{aq}) = \mu_j^0(\text{aq}) + R \cdot T \cdot \ln(m_j \cdot \gamma_j/m^0) \quad (6-2)$$

where, by definition,

$$\lim_{m_j \rightarrow 0} (m_j \rightarrow 0) \gamma_j = 1.0 \text{ at all } T \text{ and } p. \quad (6-3)$$

Hence as the solution becomes more dilute so the properties of the solute j

(and solvent; see above) approach ideal. Hence $\mu_j^0(\text{aq})$ is the chemical potential of solute j in an ideal solution ($\gamma_j = 1.0$) having unit molality. (Here and below where we do not specify a composition scale, the molality scale is implied.) It is unlikely that γ_j is unity for a real solution in which $m_j = 1 \text{ mol kg}^{-1}$.

The properties of solvent and solute (at fixed T and p) are linked through the Gibbs–Duhem equation. For a solution prepared using a single solute j and 1 kg of water;

$$(1/M_1) \cdot d\mu_1/dm_j + m_j \cdot d\mu_j/dm_j = 0 \quad (6-4)$$

If we assume that the properties of the solvent are ideal then,

$$\begin{aligned} (1/M_1) \cdot d[\mu_1^*(l) - R \cdot T \cdot M_1 \cdot m_j]/dm_j + m_j \cdot d[\mu_j^0(\text{aq}) \\ + R \cdot T \cdot \ln(m_j \cdot \gamma_j/m^0)]/dm_j = 0 \end{aligned} \quad (6-5)$$

Hence $d \ln \gamma_j / dm_j = 0$. Because, by definition, γ_j is unity when m_j is zero, γ_j is unity at all other molalities in an ideal solution. Hence if the properties of the solvent are ideal, the properties of the solute are ideal. This conclusion is relevant to our discussion concerning the change in properties of a system in the region of the cmc. To explore this point we need to develop another theme.

An explanation of why the properties of solutes deviate from ideal is based on the role of solute–solute interactions. For ionic solutes, a key contribution to these interactions is charge–charge interaction, described using the Debye–Hückel equations [17] or some variant of this treatment. For neutral solutes, solute–solute interactions can be described in terms of cosphere overlap along the lines described by Gurney [18]; see also discussion in Ref. [19]. In any event the key parameter is the distance between solute molecules in solution. A simple calculation suggested by Robinson and Stokes [17] makes the point (Table 1). We imagine a solution in which solute molecules are placed at the centres of cubes on a lattice. The distance between the (neutral) solute molecules d equals $(10^3 \cdot c \cdot N_A)^{-1/3}$ where c is the concentration expressed in mol dm^{-3} and N_A is the Avogadro constant. If c is the concentration of a 1:1 salt then d equals $(2 \cdot 10^3 \cdot c \cdot N_A)^{-1/3}$ on the grounds that each mole of salt yields on complete dissociation two moles of ions. Estimates of distance d for various concentrations c are set out in Table 1. In aqueous solutions the ‘gap’ between solute molecules is filled with water molecules, approximate diameter [20] $0.28 \times 10^{-9} \text{ m}$.

TABLE 1

Intermolecular and interionic distances for solutes (ions) in solution as a function of solute (salt) concentration

$c_j/\text{mol dm}^{-3}$	$d/10^{-9} \text{ m}$	
	Neutral solute	1:1 salt
1.0	1.18	0.94
10^{-1}	2.55	2.02
10^{-2}	5.49	4.36
10^{-3}	11.84	9.39
10^{-4}	25.50	20.25
10^{-5}	54.90	43.62

In the case of, for example, CTAB in aqueous solution [21] at a concentration (non-aggregate) of $10^{-3} \text{ mol dm}^{-3}$, the ions are approximately $9.39 \times 10^{-9} \text{ m}$ apart. But this concentration is effectively the cmc and hence after micelle formation the macroions and bromide counterions are further apart. If the aggregation number N is [2] approximately 100, the mean separation increases to $43.6 \times 10^{-9} \text{ m}$. For CTAB, part of this separation is taken up by the micelles themselves but the extent is small. For example, Tanford calculates [22] that the length of a C_{16} hydrocarbon chain is $2.0 \times 10^{-9} \text{ m}$. In other words, there are large 'patches' of water solvent between the CTAB micelles. This interesting conclusion, based on an elementary calculation, links with the comments by Shinoda [23] on the thermodynamic properties of organised solutions. Here we anticipate that the properties of both micelles and solvents in dilute micellar solutions (e.g. CTAB in aqueous solution near the cmc) are close to ideal on the grounds that if the solvent properties are ideal then so are those of the solute.

There is one more aspect which we need to discuss, again based on how we choose to describe a system. A given aqueous solution is prepared using n_1 moles of water and n_j moles of substance j . In one description we express the composition of the solution in terms of the mole fraction x_j . Then from Eq. (6-1), at fixed T and p ,

$$\mu_j(\text{aq}) = \mu_j^0(\text{aq}; \text{x-scale}) + R \cdot T \cdot \ln(x_j \cdot f_j^{\infty}) \quad (6-6)$$

In a second description, we express the composition of the solution in terms of molality, m_j . Then from Eq. (6-2) at fixed T and p , ($\mu_j^0(\text{aq})$ signals the molality scale),

$$\mu_j(\text{aq}) = \mu_j^0(\text{aq}) + R \cdot T \cdot \ln(m_j \cdot \gamma_j/m^0) \quad (6-7)$$

These two equations describe the same quantity. Therefore

$$\mu_j^0(\text{aq}; \text{x-scale}) = \mu_j^0(\text{aq}) + R \cdot T \cdot \ln(m_j \cdot \gamma_j/m^0 \cdot x_j \cdot f_j^*) \quad (6-8)$$

Both γ_j and f_j^* are defined such that as the solution becomes more dilute, both tend to unity. In the ideal solutions, $\gamma_j = f_j^* = 1.0$. The essential difference between the two standard states is the amount of solvent and solute which are mixed together to form them. Gurney [18] used the term 'cratic' to describe this difference. The claim is sometimes made that standard states defined on the mole fraction scale, called unitary quantities, are somehow more fundamental. This is not the case. However, one must be aware of the impact the various descriptions have on derived quantities. For example, because both m_j and x_j do not depend on temperature the two standard partial molar enthalpies are equal:

$$H_j^0(\text{aq}; \text{x-scale}) = H_j^0(\text{aq}) = H_j^\infty(\text{aq})$$

But the standard partial entropies differ — the mixing term.

Bearing in mind that at fixed pressure, entropy $S = -(dG/dT)$, it follows from Eq. (6-8) that,

$$S_j^0(\text{aq}; \text{x-scale}) = S_j^0(\text{aq}) + R \cdot \ln(M_1) \quad (6-9)$$

In other words, the reference partial molar entropies of the solute j differ by an amount which depends on the molar mass of the solvent.

7. SALT SOLUTIONS

The treatment in Section 6 based on Eqs. (6-1) and (6-2) was concerned with simple solutions where the solute is neutral. Here we summarise the relevant equations relating chemical potentials of both salt and solvent to the molality of a salt. In a complete analysis we would start with a consideration of electrochemical potentials but this complexity is not relevant here because we are concerned with neutral salt solutions;

i.e. the solutions have no overall electric charge. For the solvent in a salt solution where one mole of salt forms on complete dissociation v moles of ions, the chemical potential $\mu_1(\text{aq})$ of solvent water is related to the molality of salt, m_j ;

$$\mu_1(\text{aq}) = \mu_1^*(l) - v \cdot \phi \cdot R \cdot T \cdot M_1 \cdot m_j \quad (7-1)$$

For an ideal salt solution, ϕ is unity at all T and p . However, our concern is the formulation of equations for the chemical potential of salts in solution. Our plan is to summarise the descriptions for 1:1 salts (e.g. NaCl in aqueous solution) and hence develop equations for micelles formed from simple salts; e.g. CTAB micelles from $\text{RN}^+\text{Me}_3\text{Br}^-(\text{aq})$.

8. SALT SOLUTIONS: 1:1 SALTS

The starting point is an equation for the chemical potential of an ion i , charge $z_i \cdot e$, in solution (Eq. (8-1)).

$$\mu_i(\text{aq}) = \mu_i^0(\text{aq}) + R \cdot T \cdot \ln(m_i \cdot \gamma_i/m^0) \quad (8-1)$$

Here $\mu_i(\text{aq})$, $\mu_i^0(\text{aq})$ and γ_i are single ion properties, useful concepts but having limited physical significance [24]. The concepts gain significance when we combine these quantities to describe the properties of a salt in solution. For a 1:1 salt in solution, $m_2 = m_+ = m_-$. A geometric mean ionic activity coefficient is defined by $\gamma_{\pm}^2 = \gamma_+ \cdot \gamma_-$. Hence for a 1:1 salt in solution,

$$\mu_2(\text{aq}) = \mu_2^0(\text{aq}) + 2 \cdot R \cdot T \cdot \ln(m_2 \cdot \gamma_{\pm}/m^0) \quad (8-2)$$

By definition, limit ($m_2 \rightarrow 0$) $\gamma_{\pm} = 1.0$ at all T and p . Therefore, $\mu_2^0(\text{aq})$ is the chemical potential of the salt in an ideal solution ($\gamma_{\pm} = 1$) where the molality m_2 is unity. The integer '2' in Eq. (8-2) signals that one mole of salt yields with complete dissociation 2 moles of ions (= 1 mole of cations + 1 mole of anions).

9. SALT SOLUTIONS: GENERAL CASE

The pattern developed above is readily extended to other salt types. Here we consider a salt having the general formula, $v_+M^{z+} v_-X^{z-}$. With complete dissociation v moles of ions are produced in solution from one

mole of salt; $v = v_+ + v_-$. Electric neutrality is given by the condition, $|v_+ \cdot z_+| = |v_- \cdot z_-|$. The mean ionic activity coefficient, γ_{\pm} is defined by $\gamma_{\pm}^v = \gamma_+^{v_+} \cdot \gamma_-^{v_-}$. As suggested by Robinson and Stokes [17], we define a quantity Q , such that $Q^v = v_+^{v_+} \cdot v_-^{v_-}$. For solute 2 in solution,

$$\mu_2(\text{aq}) = \mu_2^0(\text{aq}) + v \cdot R \cdot T \cdot \ln(Q \cdot m_2 \cdot \gamma_{\pm}/m^0) \quad (9-1)$$

An example is interesting in the light of the discussion given below. For a salt $2M^+ X^{2-}$,

$$v = 2 + 1 = 3; \gamma_{\pm}^3 = \gamma_+^2 \cdot \gamma_-; Q^3 = 4, \text{ or } Q = 4^{(1/3)}; m_+ = 2 \cdot m_2 \text{ and } m_- = m_2.$$

Then

$$\mu_2(\text{aq}) = \mu_2^0(\text{aq}) + 3 \cdot R \cdot T \cdot \ln \{4^{(1/3)} m_2 \cdot \gamma_{\pm}/m^0\} \quad (9-2)$$

or,

$$\mu_2(\text{aq}) = \mu_2^0(\text{aq}) + R \cdot T \cdot \ln(4) + 3 \cdot R \cdot T \cdot \ln(m_2 \cdot \gamma_{\pm}/m^0) \quad (9-3)$$

The integer '3' emerges because each mole of salt produces on complete dissociation 3 moles of ions (solutes) in solution. The 'ln(4)' term is an additional but important complexity reflecting contributions of the ions to the chemical potential of the salt in solution.

10. SALT SOLUTIONS: MACROSALT

The previous two sections form an important backdrop to formulating the dependence of chemical potential for a micelle on composition, in which the micelle is treated as a charged aggregate, a macroion. We assume that each micelle is formed by aggregation of N cations having formula RN^+Me_3 to produce the cluster $(RN^+Me_3)_N$. Further $(N-\beta)$ bromide counter ions are bound to each micelle. The (electrically neutral) solute is (with $AM \equiv RNMe_3$), $\{N AM^+; (N-\beta)Br^-\}^{\beta+} \beta Br^-$. Hence the charge number for each micelle is $(\beta+)$; there are β moles of free bromide ions in solution for every mole of micelle. For an anionic micellar system (e.g. SDS), the argument runs in similar vein. The solute is $(X = \text{anion}) \beta M^+ \{(N-\beta)M^+; N X^-\}^{\beta-}$. Here we develop the arguments around the macrosalt (ms) where the macrocation (mc) is $\{N AM^+; (N-\beta)Br^-\}^{\beta+}$. For the bromide ions in solution,

$$\mu(\text{Br}^-; \text{aq}) = \mu^0(\text{Br}^-; \text{aq}) + R \cdot T \cdot \ln[m(\text{Br}^-) \cdot \gamma(\text{Br}^-)/m^0] \quad (10-1)$$

For the macrocation (mc) in solution,

$$\mu(\text{mc}; \text{aq}) = \mu^0(\text{mc}; \text{aq}) + R \cdot T \cdot \ln[m(\text{mc}) \cdot \gamma(\text{mc})/m^0] \quad (10-2)$$

Then we use the procedures outlined in Section 9. Hence,

$$\begin{aligned} \mu(\text{ms}; \text{aq}) &= \mu^0(\text{ms}; \text{aq}) \\ &+ R \cdot T \cdot \ln[m(\text{mc}) \cdot \gamma(\text{mc}) \cdot m(\text{Br}^-)^\beta \cdot \gamma(\text{Br}^-)^\beta / (m^0)^{\beta+1}] \end{aligned} \quad (10-3)$$

According to the stoichiometry; $v_+ = 1$; $v_- = \beta$ and so $v = 1 + \beta$. Further

$$Q^{(1+\beta)} = \beta^\beta \text{ and } \gamma_\pm(\text{ms}) = (\gamma_+ \cdot \gamma_-^\beta)^{1/(1+\beta)}$$

Hence,

$$\begin{aligned} \mu(\text{ms}; \text{aq}) &= \mu^0(\text{ms}; \text{aq}) \\ &+ (1 + \beta) \cdot R \cdot T \cdot \ln\{\beta^{\beta/(1+\beta)} \cdot m(\text{ms}) \cdot \gamma_\pm(\text{ms})/(m^0)\} \end{aligned} \quad (10-4)$$

Here γ_\pm is the mean ionic activity coefficient of the macrosalt in solution; $\mu^0(\text{ms}; \text{aq})$ is the chemical potential of the macrosalt in an ideal solution $\{\gamma_\pm(\text{ms}) = 1.0\}$ where the molality of the macrosalt is unity.

Equation (10-4) has an interesting structure in that an important question centres on the extent to which $(N-\beta)$ is non-zero. We can trace the argument by setting β equal to N . In other words, no counter anions are bound to the macrocation. Then

$$\begin{aligned} \mu(\text{ms}; \text{aq}) &= \mu^0(\text{ms}; \text{aq}) \\ &+ (1 + N) \cdot R \cdot T \cdot \ln[N^{N/(1+N)} \cdot m(\text{ms}) \cdot \gamma_\pm(\text{ms})/m^0] \end{aligned} \quad (10-5)$$

If N is large (e.g. close to 10^2), then

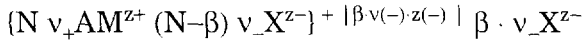
$$\begin{aligned} \mu(\text{ms}; \text{aq}) &= \mu^0(\text{ms}; \text{aq}) + N \cdot R \cdot T \cdot \ln(N) \\ &+ N \cdot R \cdot T \cdot \ln[m(\text{ms})/m^0] + N \cdot R \cdot T \cdot \ln[\gamma_\pm(\text{ms})] \end{aligned} \quad (10-6)$$

A mean quantity $\mu^0(\text{mean} - \text{ms}; \text{aq})$ is defined by the ratio $[\mu^0(\text{ms}; \text{aq})/N]$; the latter describes the effective contribution of one mole of AM^+Br^- to the standard chemical potential of the (one mole) macrosalt $\{N \cdot \text{AM}^+ N \cdot \text{Br}\}$. Hence

$$\begin{aligned} \mu(\text{ms}; \text{aq}) &= N \cdot \mu^0(\text{mean}; \text{ms}; \text{aq}) + N \cdot R \cdot T \cdot \ln(N) \\ &+ N \cdot R \cdot T \cdot \ln[m(\text{ms})/m^0] + N \cdot R \cdot T \cdot \ln[\gamma_\pm(\text{ms})] \end{aligned} \quad (10-7)$$

11. SALT SOLUTIONS: MACROSALT; GENERAL CASE

Following the case discussed above, we set down equations for a macrosalt formed by aggregation of the salt, $v_+AM^{z+} v_-X^{z-}$. We further argue that $N \cdot v_+$ moles of cations form one mole of macrocations; $(N-\beta) \cdot v_-$ moles of anions X^- are bound to one mole of macrocations leaving $|\beta \cdot v_-|$ moles of anions 'free' in solution. Hence the macrosalt is:



The electrical charge on the cation is

$$\{N \cdot v_+ \cdot z_+ + (N-\beta) \cdot v_- \cdot z_-\} = \{N \cdot (v_+ \cdot z_+ + v_- \cdot z_-) - \beta \cdot v_- \cdot z_-\} \cdot z_- \quad | \}$$

but $(v_+ \cdot z_+ + v_- \cdot z_-)$ is zero.

Hence the charge on the cation equals $|\beta \cdot v_- \cdot z_-|$ where $z_- < 0$. With complete dissociation of macrosalt into macrocation and anion, $v_+(ms) = 1$; $v_-(ms) = \beta \cdot v_-$; $v(ms) = 1 + (\beta \cdot v_-)$. Then

$$Q^{1+|\beta \cdot v_-|} = 1^1 \cdot (\beta \cdot v_-)^{\beta \cdot v_-}$$

$$\text{Also } \gamma_{\pm}(ms)^{1+|\beta \cdot v_-|} = \gamma_+(mc) \cdot \gamma_-^{\beta \cdot v_-}$$

Hence

$$\begin{aligned} \mu(ms; aq) &= \mu^0(ms; aq) \\ &+ 1 + \beta \cdot v_- \cdot R \cdot T \cdot \ln\{Q \cdot m(ms) \cdot \gamma_{\pm}(ms)/(m^0)\} \end{aligned} \quad (11-1)$$

where

$$Q = (\beta \cdot v_-)^{\beta \cdot v_- / [1 + (\beta \cdot v_-)]} \quad (11-2)$$

Hence

$$\begin{aligned} \mu(ms; aq) &= \mu^0(ms; aq) + \beta \cdot v_- \cdot R \cdot T \cdot \ln(\beta \cdot v_-) \\ &+ (1 + \beta \cdot v_-) \cdot R \cdot T \cdot \ln[m(ms)/m^0] \\ &+ (1 + \beta \cdot v_-) \cdot R \cdot T \cdot \ln[\gamma_{\pm}(ms)] \end{aligned} \quad (11-3)$$

If we assume, as before, that there is no counter-ion bonding then we can

set β equal to N . We can also assume that N is large and so we recover Eq. (10-6). Similarly for macrosalt comprising a simple cation and a macroanion (ma) in solution.

$$\begin{aligned} \mu(\text{ms}; \text{aq}) &= \mu^0(\text{ms}; \text{aq}) \\ &+ (1 + \beta \cdot v_+) \cdot R \cdot T \cdot \ln \{Q \cdot m(\text{ms}) \cdot \gamma_{\pm}(\text{ms})/(m^0)\} \end{aligned} \quad (11-4)$$

12. SALT SOLUTIONS: MOLE FRACTION SCALE

The treatment described for salts in the previous sections used the molality scale to express the composition of a given salt solution. We may, of course, use the mole fraction scale. Hence Eq. (9-1) would be written in the following form for a salt, substance 2.

$$\mu_2(\text{aq}) = \mu_2^0(\text{aq}; \text{x-scale}) + v \cdot R \cdot T \cdot \ln(Q \cdot x_2 \cdot f_{\pm}^*/m^0) \quad (12-1)$$

where at all T and p , $\lim(x_2 \rightarrow 0) f_{\pm}^* = 1.0$. Hence $\mu_2^0(\text{aq}; \text{x-scale})$ is the chemical potential of salt 2 in an ideal ($f_{\pm}^* = 1.0$) aqueous solution where x_2 is unity. Thus $\mu_2^0(\text{aq}; \text{x-scale}) \neq \mu_2^0(\text{aq})$, the difference being a cratic contribution (Section 6).

13. MICELLAR EQUILIBRIA: PHASE EQUILIBRIA

In Section 2 we argued that if micelle formation can be described in terms of thermodynamic equilibrium, we need to formulate the chemical potentials of substances involved in these equilibria in terms of the composition of the system. For example, with reference to Eq. (2-1), we require equations for the chemical potentials of the salt AM^+Br^- in solution and the micelles in the system. The phase equilibrium model writes Eq. (2-1) in terms of a salt in solution and the pure micellar phase (at fixed T and p). Thus,

$$N \cdot \mu(\text{AM}^+\text{Br}^-; \text{aq}) = \mu^* \{(\text{AM}^+\text{Br}^-)_N; \text{pure}\} \quad (13-1)$$

The symbol $*$ indicates a pure phase. In these terms the micelles form a separate phase dispersed through the aqueous solution containing the simple salt AM^+Br^- . The closest textbook analogy to this approach is the

treatment of the dependence of solubilities of sparingly soluble salts on ionic strength. We illustrated this point in Section 2 with reference to an aqueous system prepared using water and AgCl(s).

The state AgCl(s) is, of course, familiar whereas the state $((\text{AM}^+\text{Br}^-)_\text{N}; \text{pure})$ is not. However, proceeding on the basis of the condition set out in Eq. (13-1), we incorporate the composition as follows based on the (equilibrium) critical micellar molality, cmm .

$$\begin{aligned} N \cdot \mu^0(\text{AM}^+\text{Br}^-; \text{aq}) + 2 \cdot N \cdot R \cdot T \ln [\text{cmm}(\text{AM}^+\text{Br}^-) \cdot \gamma_{\pm}(\text{AM}^+\text{Br}^-)/m^0] \\ = \mu^*[(\text{AM}^+\text{Br}^-)_\text{N}; \text{pure}] \end{aligned} \quad (13-2)$$

Then by definition (at temperature T),

$$\Delta_{\text{mic}} G^0(\text{pe}) = \mu^*[(\text{AM}^+\text{Br}^-)_\text{N}; \text{pure}] - N \cdot \mu^0(\text{AM}^+\text{Br}^-; \text{aq}) \quad (13-3)$$

$\Delta_{\text{mic}} G^0(\text{pe})$ is the standard increase in Gibbs energy when N moles of salt AM^+Br^- in an ideal solution ($\gamma_{\pm} = 1$) forms one mole of pure micelle; 'pe' signals the phase equilibrium model. Hence,

$$\Delta_{\text{mic}} G^0(\text{pe}) = 2 \cdot N \cdot R \cdot T \cdot \ln \{ \text{cmm}(\text{AM}^+\text{Br}^-) \cdot \gamma_{\pm}(\text{AM}^+\text{Br}^-)/m^0 \} \quad (13-4)$$

The integer '2' emerges from the fact that AM^+Br^- is a 1:1 salt. Unfortunately, we do not always know the aggregation number N. By definition,

$$\Delta_{\text{mic}} G^0(\text{N}; \text{pe}) = \Delta_{\text{mic}} G^0(\text{pe})/N$$

Hence

$$\Delta_{\text{mic}} G^0(\text{N}; \text{pe}) = 2 \cdot R \cdot T \cdot \ln \{ \text{cmm}(\text{AM}^+\text{Br}^-) \cdot \gamma_{\pm}(\text{AM}^+\text{Br}^-)/m^0 \} \quad (13-5)$$

Therefore $\Delta_{\text{mic}} G^0(\text{N}; \text{pe})$ is the standard increase in Gibbs energy when one mole of salt AM^+Br^- in its solution standard state contributes to the formation of pure micelle, $(\text{AM}^+\text{Br}^-)_\text{N}$. If the solution is dilute then $\gamma_{\pm}(\text{AM}^+\text{Br}^-) \cong 1.0$. Hence,

$$\Delta_{\text{mic}} G^0(\text{N}; \text{pe}) = 2 \cdot R \cdot T \cdot \ln \{ \text{cmm}(\text{AM}^+\text{Br}^-)/m^0 \} \quad (13-6)$$

If the aqueous solution is dilute the ratio cmm/m^0 is approximately equal to cmc/c_r where $c_r = 1 \text{ mol dm}^{-3}$.

Hence,

$$\Delta_{\text{mic}}G^0(N; \text{pe}) = 2 \cdot R \cdot T \cdot \ln \{c_{\text{mc}}(AM^+Br^-)/c_r\} \quad (13-7)$$

The term c_r is usually omitted but when included it has the advantage of removing questions about the logarithm of a unit.

Equation (13-7) is the classic 'Phase Equilibrium' equation and it is important to recall the standard states used in the derivation of this equation; i.e. pure micelle and an ideal salt solution. But granted the validity of the model, measurement of the cmc yields $\Delta_{\text{mic}}G^0(N; \text{pe})$. The only real problem concerned the aggregation number but the difficulty was overcome by dividing through by N . An apparent advantage of the PE model is that there is no composition variable for the micellar phase. The standard state for the micellar phase is almost hidden within the term $\Delta_{\text{mic}}G^0(N; \text{pe})$ (cf. Eq. (13-3)) but, as we stress below, must not be overlooked. In fact, by hiding these terms it could be argued that we avoid problems. Certainly the final equation has an attractive simplicity.

14. MICELLAR EQUILIBRIA: PHASE EQUILIBRIA; GENERAL CASE

The analysis outlined in the previous section is readily extended to more complicated macrosalts. For the macrosalt, $v_+AM^{z+} v_-X^{z-}$ (cf. Section 11), we write the micellar equilibrium in the following form (at fixed T and p).

$$N \cdot \mu(v_+AM^{z+} v_-Br^{z-}; \text{aq}) = \mu^* \{\text{pure micelle}\} \quad (14-1)$$

Then from Eq. (11-4)

$$N \cdot \mu_2^0(\text{aq}) + v \cdot N \cdot R \cdot T \cdot \ln (Q \cdot c_{\text{mm}} \cdot \gamma_{\pm}/m^0) = \mu^* (\text{pure micelle}) \quad (14-2)$$

By definition,

$$\Delta_{\text{mic}}G^0(N; \text{pe}) = [\mu^* (\text{pure micelle})/N] - \mu_2^0(\text{aq})$$

Hence,

$$\Delta_{\text{mic}}G^0(N; \text{pe}) = v \cdot R \cdot T \cdot \ln (Q \cdot c_{\text{mm}} \cdot \gamma_{\pm}/m^0) \quad (14-3)$$

If the solution is dilute,

$$\Delta_{\text{mic}}G^0(\text{N}; \text{pe}) = v \cdot R \cdot T \cdot \ln (Q \cdot \text{cmc}/c_r) \quad (14-4)$$

Hence in the case of micelles formed by a 2:1 electrolyte, $\text{AM}^{2+} 2\text{Br}^-$ (see, for example, Ref. [25]),

$$\Delta_{\text{mic}}G^0(\text{N}; \text{pe}) = 3 \cdot R \cdot T \cdot \ln [(4)^{1/3} \cdot \text{cmc}/c_r] \quad (14-5)$$

or,

$$\Delta_{\text{mic}}G^0(\text{N}; \text{pe}) = R \cdot T \cdot \ln (4) + 3 \cdot R \cdot T \cdot \ln [\text{cmc}/c_r] \quad (14-6)$$

The term $R \cdot T \cdot \ln(4)$ at 298.2 K contributes 3.4 kJ mol^{-1} to the calculated $\Delta_{\text{mic}}G^0(\text{N}; \text{pe})$ and is therefore not negligible.

15. MICELLAR EQUILIBRIA: PHASE EQUILIBRIUM; MOLE FRACTION SCALE

In a development of the condition in Eq. (14-1), we could describe the composition of the solution in terms of mole fraction of the salt. Then the analogue of Eq. (14-2) is as follows; (cf. Eq. (12-1))

$$\begin{aligned} N \cdot \mu_2^0(v_+ \text{AM}^{z+} v_- \text{X}^{z-}; \text{aq}; \text{x-scale}) + v \cdot N \cdot R \cdot T \cdot \ln (Q \cdot \text{cmx} \cdot f_{\pm}^*) \\ = \mu^* (\text{pure micelle}) \end{aligned} \quad (15-1)$$

Here cmx is the equilibrium mole fraction of the salt at the critical micellar mole fraction and f_{\pm}^* is the mean ionic activity coefficient for the salt in solution at the composition, cmx .

By definition

$$\begin{aligned} \Delta_{\text{mic}}G^0(\text{N}; \text{pe}; \text{x-scale}) = [\mu^* (\text{pure micelle})/N] \\ - \mu_2^0(v_+ \text{AM}^{z+} v_- \text{X}^{z-}; \text{aq}; \text{x-scale}) \end{aligned} \quad (15-2)$$

If the solution is dilute, $f_{\pm}^* \cong 1.0$. Then

$$\Delta_{\text{mic}}G^0(\text{N}; \text{pe}; \text{x-scale}) = v \cdot R \cdot T \cdot \ln(Q \cdot \text{cmx}) \quad (15-3)$$

Hence for a 1:1 salt ($Q = 1$),

$$\Delta_{\text{mic}}G^0(\text{N}; \text{pe}; \text{x-scale}) = 2 \cdot R \cdot T \cdot \ln(\text{cmx}) \quad (15-4)$$

Clearly, $\Delta_{\text{mic}}G^0(\text{N}; \text{pe}; \text{x-scale})$ differs from that defined on the molality scale, $\Delta_{\text{mic}}G^0(\text{N}; \text{pe})$, the difference being a cratic term. This does not mean that $\Delta_{\text{mic}}G^0(\text{N}; \text{pe}; \text{x-scale})$ is somehow more fundamental.

Van Os and coworkers use Eq. (15-4) in an examination of data for alkylbenzene-sulphonates [26]. They comment that the analysis does not take account of counter-ion binding. Actually the model itself rules out consideration of such effects unless one argues that the binding is 100% in forming a neutral micellar phase.

16. MICELLAR EQUILIBRIA: LIQUID MIXTURE MODEL

This model, a development of the Phase Equilibrium Model, is based on the treatment of the thermodynamic properties of liquid mixtures. A solution is prepared by adding n_j moles of surfactant to water. At the cmx, the equilibrium mole fraction of micelles present in the aqueous solution is x_m . The chemical potential of micelles is related through x_m to the chemical potential of pure micellar phase, $\mu^0(\text{pure micelle})$ at the same T and p. Then

$$\mu(\text{micelle}; \text{aq}) = \mu^*(\text{pure micelle}) + R \cdot T \cdot \ln(x_m \cdot f_m) \quad (16-1)$$

where limit $(x_m \rightarrow 1) f_m = 1.0$ at all T and p.

A close analogy to Eq. (16-1) is an equation describing the chemical potential of ethanol in a binary mixture, water + ethanol, in terms of the mole fraction of ethanol and the chemical potential of pure ethanol at the same T and p. The analogue of Eq. (15-1) using the mole fraction scale for both micelles and salt, $v_+AM^{z+} v_-X^{z-}$ is as follows.

$$\begin{aligned} N \cdot \mu_2^0(v_+AM^{z+} v_-X^{z-}; \text{aq}; \text{x-scale}) + v \cdot N \cdot R \cdot T \cdot \ln(Q \cdot \text{cmx} \cdot f_+^*) \\ = \mu^*(\text{pure micelle}) + R \cdot T \cdot \ln(x_m \cdot f_m) \end{aligned} \quad (16-2)$$

In contrast to Eq. (14-2) we have a term on the right hand side of Eq. (16-2) in a composition variable, x_m . Rather like the case of ethanol in an ethanol + water mixture, we have not specified the nature (structure) of the micelle in the aqueous solution, mole fraction x_m . By definition,

$$\begin{aligned} \Delta_{\text{mic}}G^0(\text{N}; \text{liq. mix}; \text{x-scale}) = [\mu^*(\text{pure micelle}) / N] \\ - \mu_2^0(v_+AM^{z+} v_-X^{z-}; \text{aq}; \text{x-scale}) \end{aligned} \quad (16-3)$$

Then

$$\Delta_{\text{mic}}G^0(\text{N}; \text{liq. mix; x-scale}) = v \cdot R \cdot T \cdot \ln(Q \cdot \text{cmx} \cdot f_{\pm}^*) - (R \cdot T/N) \cdot \ln(x_m \cdot f_m) \quad (16-4)$$

If the solution is dilute in salt, $v_+AM^{z+} v_-X^{z-}$, we can set f_{\pm}^* to unity. The term f_m is troublesome because if the solution is dilute, the system is far from pure micelle in composition terms. Clearly we cannot set f_m to unity and we have little idea what its value might be. Based on a simple system such as THF + water (see above) we expect f_m to differ significantly from unity. As Kresheck comments [1] the usual approach assumes that the second term on the right hand side of Eq. (16-4) is negligibly small as a consequence of the large aggregation number. Then for a 1:1 salt, AM^+X^- , in dilute solution,

$$\Delta_{\text{mic}}G^0(\text{N}; \text{liq. mix; x-scale}) = 2 \cdot R \cdot T \cdot \ln(\text{cmx}) \quad (16-5)$$

This equation has the same form as Eq. (15-4) although the starting models differ. What happened was that we kept the same standard states and dropped the last troublesome term in Eq. (16-4) by dividing by a large aggregation number. But as noted above, we have not described in the present context the state of the micelles in the aqueous solution. The division by N is indeed welcome if only in the context of obtaining an estimate of $\Delta_{\text{mic}}G^0(\text{N}; \text{liq. mix; x-scale})$ from cmx .

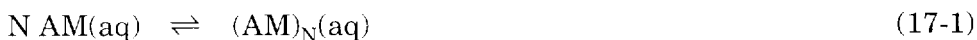
For non-ionic surfactants, the analogue of Eq. (16-4) can be written in the following form.

$$\Delta_{\text{mic}}G^0(\text{N}; \text{liq. mix; x-scale}) = R \cdot T \cdot \ln(\text{cmx}) - (R \cdot T/N) \cdot \ln(x_m) \quad (16-6)$$

Here we have assumed that for the non-ionic systems the two activity coefficients are unity. Equation (16-5) is similar to that quoted by Abramzon [27] who argues that the basis is the 'laws of heterogeneous equilibrium'. In other words, the micelles form a microphase. Actually the argument used by Abramzon switches to the phase equilibrium model discussed in Section 13 because at this point he argues that x_m is unity (stated to be an assumption). Without this switch no further progress can be made unless one follows the argument given by Kresheck [1] that $(1/N) \cdot \ln(x_m)$ is negligible, retaining the liquid mixture approach. In any event, the reference state is the pure micellar phase.

17. MASS ACTION MODEL: NEUTRAL SOLUTES

The Phase Equilibrium model is based on a description using Eq. (2-1). The model made progress by treating the micelles as a separate phase to that of aqueous solutions containing the simple salt AM^+X^- . In the Mass Action model, both micelles and the salt are treated as solutes in an aqueous solution. To develop the argument, we consider first the simple case of a neutral solute AM . At the cmc, N moles of these solutes cluster to form one mole of neutral micelle, $(AM)_N$ [28]. The chemical equilibrium has the following form.



Hence at equilibrium, characterised by the equilibrium mole fractions $x^{eq}(AM)$ and $x^{eq}\{(AM)_N\}$,

$$N \cdot \mu^{eq}(AM; aq) = \mu^{eq}\{(AM)_N; aq\} \quad (17-2)$$

We stress that both AM and $(AM)_N$ are solutes in an aqueous solution. Hence using Eq. (5-1) for the mole fraction scale [22].

$$\begin{aligned} N \cdot \mu^0(AM; x\text{-scale}; aq) + N \cdot R \cdot T \cdot \ln[cmx \cdot f(AM)^*] \\ = \mu^0[(AM)_N; x\text{-scale}; aq] + R \cdot T \cdot \ln[x(AM)_N \cdot f(AM_N)^*] \end{aligned} \quad (17-3)$$

By definition, (ma = Mass Action model)

$$\begin{aligned} \Delta_{mic}G^0(N; ma; x\text{-scale}) = R \cdot T \cdot \ln[cmx \cdot f(AM)^*] \\ - (R \cdot T/N) \cdot \ln[x(AM)_N \cdot f(AM_N)^*] \end{aligned} \quad (17-4)$$

As commented above, both monomers and micelles are in aqueous solution. Hence, a self-consistent approximation sets, $f(AM)^* = f(AM_N)^* = 1.0$ for dilute solutions on the grounds that the properties of neutral solutes in dilute solutions are close to ideal. Consistent with the arguments outlined above, we assume that N is large and hence the term, $(R \cdot T/N) \cdot \ln[x(AM)_N \cdot f(AM_N)^*]$ is negligibly small. Hence,

$$\Delta_{mic}G^0(N; ma; x\text{-scale}) = R \cdot T \cdot \ln(cmx) \quad (17-5)$$

The latter equation is in the required form for the calculation of $\Delta_{mic}G^0(N; ma; x\text{-scale})$ from the measured cmx . The standard states for both simple

and micellar solutes are ideal aqueous solutions. The absence of a simple integer in Eq. (17-5) comes about from the fact that each mole of monomer AM produces one mole of solute AM in solution. In other words, Eq. (17-5) is not appropriate for polar amphiphiles. The molality scale equivalent of Eq. (17-5) is as follows:

$$\begin{aligned}\Delta_{\text{mic}}G^0(\text{N}; \text{ma}) &= \mu^0[(\text{AM})_{\text{N}}; \text{aq}]/\text{N} - \mu^0[\text{AM}; \text{aq}] \\ &= \text{R} \cdot \text{T} \cdot \ln(\text{cmm}/\text{m}^0)\end{aligned}\quad (17-6)$$

18. CONTROVERSY

Equation (17-5) has a simple form. But something rather worrying has emerged. It is not a difficult task bearing in mind what has gone before to rewrite Eq. (17-5) to describe the following phase equilibrium condition.

$$\text{N} \cdot \mu^{\text{eq}}(\text{AM}; \text{aq}) = \mu^* \{\text{pure micelle}\} \quad (18-1)$$

Then,

$$\begin{aligned}\Delta_{\text{mic}}G^0(\text{pe}; \text{N}; \text{x-scale}) &= \mu^* (\text{pure micelle})/\text{N} - \mu^0[\text{AM}; \text{aq}; \text{x-scale}] \\ &= \text{R} \cdot \text{T} \cdot \ln(\text{cmx})\end{aligned}\quad (18-2)$$

Here we have assumed that the aqueous solution is dilute; i.e. $f(\text{AM}; \text{aq})^* = 1.0$. At this stage we compare Eqs. (17-5) and (18-2). According to the analysis, a measurement of cmx for a given system leads to either $\Delta_{\text{mic}}G^0(\text{ma}; \text{N}; \text{x-scale})$ or $\Delta_{\text{mic}}G^0(\text{pe}; \text{N}; \text{x-scale})$. This could be taken to mean that the chemical potentials of micelles under both descriptions are equal; i.e. the claim is that $\mu^0(\text{AM}_{\text{N}}; \text{x-scale}; \text{aq}) = \mu^*[\text{AM}; \text{pure micelle}]$. This cannot be correct. It requires that the transfer standard chemical potential of one mole of micelles from the pure micelle phase into an ideal aqueous solution at unit mole fraction is zero. Without experimental evidence that this is so, our argument has derailed somewhere. Suspicion falls on the Phase Equilibrium model of the type expressed in Eq. (18-1). To have a realistic basis, the thermodynamic condition and its development must have an element of realism. The question centres on the extent to which the solution of salt (Eq. (18-1)) or simple solute (cf. Eq. (18-1)) at the mole fraction cmx would be at equilibrium with the micellar phase. So returning to Eqs. (13-1) and (18-1), we introduced one assumption

concerning the reality of the micellar phase and another assumption that the equilibrium holds at the mole fraction, cmx . There are no grounds for the latter assumption. In fact, the assumption involves an intermediate step which transfers pure micelles (Eq. (17-1)) into the substance $(AM)_N$ in Eq. (18-1). Broadly speaking, we have to rewrite Eq. (18-2) in the following form.

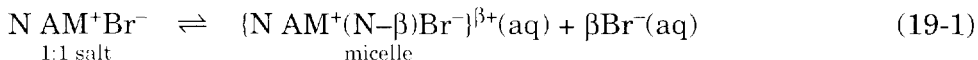
$$\Delta_{mic} G^0(pe; N; x\text{-scale}) = \Delta[\text{pure micelle} \rightarrow (AM)_N(aq)] \mu^0/N + R \cdot T \cdot \ln(cmx) \quad (18-3)$$

Here $\Delta[\text{pure micelle} \rightarrow (AM)_N(aq)] \mu^0$ is the standard transfer chemical potential of pure micelles to form aggregates AM_N in aqueous solution.

The analysis therefore throws doubt on the classic phase equilibrium model. However, a transfer parameter may correct the errors implicit in the analysis. We return below to this point.

19. MASS ACTION MODEL: SALT SOLUTIONS; 1:1 SALTS

We turn attention to application of the Mass Action Model to solutions prepared using, for example, the salt AM^+Br^- . The analysis is based on the equations developed in Section 8. The key assumption is that at the cmm, there exists an equilibrium having the following form.



This equilibrium is not envisaged to hold at any molality except the cmm. In the solution the micelles have charge number $+\beta$ such that $(N-\beta)$ moles of anions are bound to N moles of cations in the micelles, β moles of bromide ions being free in solution. This formulation is similar to that used by Woolley and coworkers [29,30]. The thermodynamic condition in Eq. (19-1) is re-expressed (at temperature T) in terms of chemical potentials; mc = macrocation.

$$N \cdot \mu(AM^+Br^-; aq) = \mu(mc; aq) + \beta \cdot \mu(Br^-; aq) \quad (19-2)$$

The left hand side of this equation contains the chemical potential of a 1:1 salt. On the right hand side are two single ion chemical potentials. It

is useful to leave the latter in this form with the proviso that we do not violate the condition of electric neutrality. Hence,

$$\begin{aligned} N \cdot \mu^0(\text{AM}^+\text{Br}^-; \text{aq}) + 2 \cdot N \cdot R \cdot T \cdot \ln[m(\text{AM}^+\text{Br}^-) \cdot \gamma_{\pm}(\text{AM}^+\text{Br}^-)/m^0]^{\text{eq}} \\ = \mu^0(\text{mc}; \text{aq}) + R \cdot T \cdot \ln[m(\text{mc}) \cdot \gamma(\text{mc})/m^0]^{\text{eq}} \\ + \beta \cdot \mu^0(\text{Br}^-; \text{aq}) + \beta \cdot R \cdot T \cdot \ln[m(\text{Br}^-)/m^0]^{\text{eq}} \end{aligned} \quad (19-3)$$

By definition, the standard Gibbs energy for the formation of one mole of $[\{N \text{AM}^+(\text{N}-\beta) \text{Br}^-\}^{\beta+} \beta \text{Br}^-](\text{aq})$ from N moles of $\text{AM}^+\text{Br}^-(\text{aq})$ according to the mass action (ms) model,

$$\Delta_{\text{mic}}G^0(\text{ma}) = \mu^0(\text{mc}; \text{aq}) + \beta \cdot \mu^0(\text{Br}^-; \text{aq}) - N \cdot \mu^0(\text{AM}^+\text{Br}^-; \text{aq}) \quad (19-4)$$

or,

$$\Delta_{\text{mic}}G^0(\text{ma}) = \mu^0(\text{mc}; \text{aq}) - N \cdot \mu^0(\text{AM}^+; \text{aq}) - (\text{N}-\beta) \cdot \mu^0(\text{Br}^-; \text{aq}) \quad (19-5)$$

Hence from Eq. (19-3) (we drop the 'eq' superscript which we assume is implicit in the following)

$$\begin{aligned} \Delta_{\text{mic}}G^0(\text{ma}) = 2 \cdot N \cdot R \cdot T \cdot \ln[m(\text{AM}^+\text{Br}^-) \cdot \gamma_{\pm}(\text{AM}^+\text{Br}^-)/m^0] \\ - R \cdot T \cdot \ln[m(\text{mc}) \cdot \gamma(\text{mc})/m^0] \\ - \beta \cdot R \cdot T \cdot \ln[m(\text{Br}^-) \cdot \gamma(\text{Br}^-)/m^0] \end{aligned} \quad (19-6)$$

A little rearrangement yields the following equation.

$$\begin{aligned} \Delta_{\text{mic}}G^0(\text{ma})/R \cdot T = 2 \cdot N \cdot \ln[m(\text{AM}^+\text{Br}^-)/m^0] \\ - \beta \cdot \ln[m(\text{Br}^-)/m^0] - \ln[m(\text{mc})/m^0] \\ + \ln[\gamma_{\pm}(\text{AM}^+\text{Br}^-)^{2N}/\gamma(\text{mc}) \cdot \gamma(\text{Br}^-)] \end{aligned} \quad (19-7)$$

But for a 1:1 salt, $m(\text{AM}^+) = m(\text{Br}^-) = m(\text{AM}^+\text{Br}^-)$. Then

$$\begin{aligned} \Delta_{\text{mic}}G^0(\text{ma})/R \cdot T = N \cdot \ln[m(\text{AM}^+)/m^0] + N \cdot \ln[m(\text{Br}^-)/m^0] \\ - N \cdot \ln[m(\text{Br}^-)/m^0] - \ln[m(\text{mc})/m^0] \\ + \ln[\gamma_{\pm}(\text{AM}^+\text{Br}^-)^{2N}/\gamma(\text{mc}) \cdot \gamma(\text{Br}^-)] \end{aligned} \quad (19-8)$$

But at the equilibrium point, $m(\text{AM}^+) = m(\text{Br}^-) = \text{cmm}$. Therefore,

$$\begin{aligned} \Delta_{\text{mic}}G^0(\text{ma})/R \cdot T = \ln[(\text{cmm})^N \cdot (\text{cmm})^N \cdot (\text{cmm})^{-\beta}/(m^0)^{2N-\beta}] \\ - \ln[m(\text{mc})/m^0] + \ln[\gamma_{\pm}(\text{AM}^+\text{Br}^-)^{2N}/\gamma(\text{mc}) \cdot \gamma(\text{Br}^-)] \end{aligned} \quad (19-9)$$

$\Delta_{\text{mic}}G^0$ measures the difference between the standard chemical potentials of the solutes $\text{AM}^+\text{Br}^-(\text{aq})$ and $\{\text{N AM}^+ (\text{N}-\beta)\text{Br}^-\}^{\beta+} \beta\text{Br}^-(\text{aq})$. As described above, we define a new quantity describing the standard increase in Gibbs energy when one mole of AM^+Br^- forms a micelle.

$$\Delta_{\text{mic}}G^0(\text{ma}; \text{N}) = \Delta_{\text{mic}}G^0(\text{ma}) / \text{N}$$

Then

$$\Delta_{\text{mic}}G^0(\text{ma}; \text{N}) / \text{R} \cdot \text{T} = [2 - (\beta/\text{N})] \cdot \ln[(\text{cmm})/\text{m}^0] - (1/\text{N}) \cdot \ln[\text{m}(\text{mc})/\text{m}^0] + (1/\text{N}) \cdot \ln[\gamma_{\pm}(\text{AM}^+\text{Br}^-)^{2\text{N}} / \gamma(\text{mc}) \cdot \gamma(\text{Br}^-)] \quad (19-10)$$

At this stage we make several by now familiar assumptions:

- (I) The term $(1/\text{N}) \cdot \ln[\text{m}(\text{mc})/\text{m}^0]$ is negligibly small because the molality of the macrocation is small and N is usually large.
- (II) The solution is dilute in both simple salt and macrosalt such that $\gamma_{\pm}(\text{AM}^+\text{Br}^-) = \gamma(\text{mc}) = \gamma(\text{Br}^-) = 1.0$. Hence,

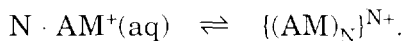
$$\Delta_{\text{mic}}G^0(\text{ma}; \text{N}) = \text{R} \cdot \text{T} \cdot [2 - (\beta/\text{N})] \cdot \ln[(\text{cmm})/\text{m}^0] \quad (19-11)$$

Two limiting conditions are identified:

- (I) No counterions are bound to the micelle such that the micellar state is $[\text{N} \cdot \text{AM}^+]$; i.e. $\beta = \text{N}$ (see, for example, Ref. [31]). Hence,

$$\Delta_{\text{mic}}G^0(\text{ma}; \text{N}) = \text{R} \cdot \text{T} \cdot \ln[\text{cmm}/\text{m}^0] \quad (19-12)$$

Not unexpectedly, we recover Eq. (17-6) for the equilibrium,



The $(\text{N} \cdot \text{Br}^-)$ ions are, in these terms, passive.

- (II) All counter ions are bound to the micelles such that β is zero and each micelle has zero electric charge. Hence,

$$\Delta_{\text{mic}}G^0(\text{ma}; \text{N}) = 2 \cdot \text{R} \cdot \text{T} \cdot \ln[\text{cmm}/\text{m}^0] \quad (19-13)$$

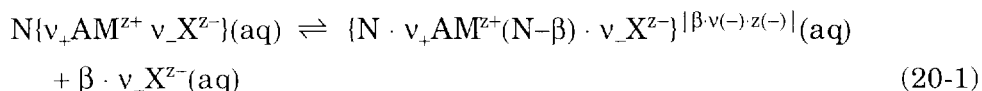
At this stage, it is informative to re-examine the first assumption described following Eq. (19-10). For a micelle formed by a 1:1 salt where the cmc is $10^{-4} \text{ mol dm}^{-3}$, $\Delta_{\text{mic}}G^0(\text{ma}; \text{N}) / \text{R} \cdot \text{T}$ is -18.42 . The term $(1/\text{N}) \cdot \ln[\text{m}(\text{mc})/\text{m}^0]$ requires an estimate of the molality of micelle present at the cmc. This molality cannot be zero otherwise (see Eq. (19-10)) $\Delta_{\text{mic}}G^0(\text{ma}; \text{N}) / \text{R} \cdot \text{T}$ is positive infinite. If $\text{m}(\text{mc})$ is $10^{-10} \text{ mol kg}^{-1}$, the term $(1/\text{N})$

$\ln(m(\text{mc})/m^0)$ increases $\Delta_{\text{mic}}G^0(\text{ma}; N)$ by 0.23 assuming N is 100. If $m(\text{mc})$ equals $10^{-30} \text{ mol dm}^{-3}$ the term increases $\Delta_{\text{mic}}G^0(\text{ma}; N)/R \cdot T$ by 0.69. Hence the $\Delta_{\text{mic}}G^0(\text{ma}; N)$ calculated using Eq. (19-13), for $\text{cmm} < 1 \text{ mol kg}^{-1}$, is slightly too negative.

Bearing in mind the discussion in Section 18, we are not too surprised to discover that we have obtained an equation (19-13) having the same right hand side as Eq. (13-8) derived using the phase equilibrium model even though the standard state for the micelles is quite different. Again we suggest that the reason for this similarity is the unrealistic treatment of the condition in Eq. (13-1). To repeat the point in Section 18, there is no guarantee that the composition of a solution at equilibrium with the pure micellar phase is close to the critical micellar composition. The apparent similarities between the two final equations are not a result of the assumptions listed after Eq. (19-11).

20. MASS ACTION MODEL: IONIC SOLUTES; POLYVALENT IONS

We develop the argument along the lines described in the previous section except that the charge numbers on the ions are not restricted to unity. Hence the equation for micelle formation (cf. Eq. (19-2)) has the following form:



In the absence of micelle formation the salt, $v_+AM^{z+} v_-X^{z-}$, produces with complete dissociation $v (= v_+ + v_-)$ moles of ions in solution. On micelle formation, N moles of cations cluster with $(N-\beta) \cdot v_-$ moles of anions bound to the micelles. The charge on each micelle is $|\beta \cdot v_- \cdot z_-|$. The equilibrium discussed in Section 14 is expressed in terms of chemical potentials using Eq. (10-4); mc = macrocation.

$$N \cdot \mu[\{v_+AM^{z+} v_-X^{z-}\}(\text{aq})] = \mu(\text{mc}; \text{aq}) + \beta \cdot v_- \cdot \mu(X^{z-}; \text{aq}) \quad (20-2)$$

At the equilibrium critical micellar composition, the molality of the salt is cmm ; the molalities of cations and anions are $v_+ \cdot \text{cmm}$ and $v_- \cdot \text{cmm}$ respectively. The molality of the macrocation at the critical micellar composition is $m(\text{mc})$, activity coefficient $\gamma_+(\text{mc})$.

Then

$$\begin{aligned}
 N \cdot \mu^0[\{v_+ AM^{z+} v_- X^{z-}\}(aq)] + N \cdot v \cdot R \cdot T \cdot \ln [Q(\text{salt}) \cdot cmm \cdot \gamma_{\pm}/m^0] \\
 = \mu^0(mc; aq) + R \cdot T \cdot \ln[m(mc) \cdot \gamma_+(mc)/m^0] \\
 + \beta \cdot v_- \cdot \{\mu^0(X^{z-}; aq) + R \cdot T \cdot \ln [v_- \cdot cmm \cdot \gamma_-(X^{z-})/m^0]\}
 \end{aligned} \quad (20-3)$$

By definition,

$$\begin{aligned}
 \Delta_{\text{mic}} G^0/R \cdot T = \mu^0(mc; aq) + \beta \cdot v_- \cdot [\mu^0(X^{z-}; aq) \\
 - N \cdot \mu^0[\{v_+ AM^{z+} v_- X^{z-}\}(aq)]
 \end{aligned} \quad (20-4)$$

Then,

$$\begin{aligned}
 \Delta_{\text{mic}} G^0/R \cdot T = N \cdot v \cdot \ln [Q(\text{salt}) \cdot cmm/m^0] \\
 - \beta \cdot v_- \cdot \ln [v_- \cdot cmm/m^0] - \ln[m(mc)/m^0] \\
 + \ln[\gamma_{\pm}^{N \cdot v}/\gamma_+(mc) \cdot \gamma_-(X^{z-})^{\beta \cdot v(-)}]
 \end{aligned} \quad (20-5)$$

We have established a procedure for defining a quantity $\Delta_{\text{mic}} G^0(N)$. Then,

$$\begin{aligned}
 \Delta_{\text{mic}} G^0(N)/R \cdot T = \ln [Q(\text{salt}) - \beta \cdot v_-/N] \cdot \ln(v_-) \\
 + [v - (\beta \cdot v_-/N)] \cdot \ln[cmm/m^0] - (1/N) \cdot \ln[m(mc)/m^0] \\
 + (1/N) \cdot \ln[\gamma_{\pm}^{N \cdot v}/\gamma_+(mc) \cdot \gamma_-(X^{z-})^{\beta \cdot v(-)}]
 \end{aligned} \quad (20-6)$$

We now make several assumptions consistent with points made in previous sections concerning systems where N is large.

- (i) The solution is ideal; $\gamma_{\pm} = \gamma_+(mc) = \gamma_-(X^{z-}) = 1.0$.
- (ii) $(1/N) \cdot \ln[m(mc)/m^0]$ is negligibly small.
- (iii) $(\beta \cdot v_-/N) \cdot \ln(v_-)$ is negligibly small.
- (iv) $(\beta \cdot v_-/N) \cdot \ln[cmm/m^0]$ is negligibly small.

Hence,

$$\Delta_{\text{mic}} G^0(N) = v \cdot R \cdot T \cdot \ln[Q(\text{salt}) \cdot cmm/m^0] \quad (20-7)$$

For a 1:1 salt, $v = 2$ and $Q = 1$. But for other systems, the stoichiometric parameters are important. An example is useful here. Devinsky et al. [32] report details of micelle formation by bis-quaternary salts in aqueous solutions. For these systems, $v = 3$, $v_+ = 1$ and $v_- = 2$ and hence $Q^3 = 4$. Then for the surfactant where $cmm = 2 \times 10^{-3} \text{ mol kg}^{-1}$ at 298.2 K.

$$\Delta_{\text{mic}} G^0(N) = 3 \cdot R \cdot T \cdot \ln[4 \times 2.0 \times 10^{-3}] = -35.95 \text{ kJ mol}^{-1}$$

Devinsky et al. use Eq. (19-13) which yields $-15.4 \text{ kJ mol}^{-1}$, a serious underestimate. Similarly, for disodium 2-octadecyl-1,3-propandyl bisulfate at 55 Celsius [33] the cmc is $2.39 \times 10^{-3} \text{ mol dm}^{-3}$. Hence,

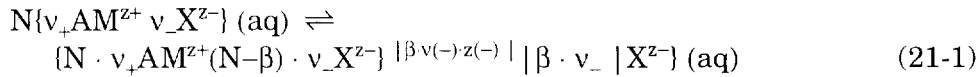
$$\Delta_{\text{mic}} G^0(\text{ma}; N) = 3 \cdot R \cdot T \cdot \ln(4 \times 2.39 \times 10^{-3})$$

or

$$\Delta_{\text{mic}} G^0(\text{ma}; N) = -38.04 \text{ kJ mol}^{-1}.$$

21. MASS ACTION MODEL: MACROMOLECULAR SALT; GENERAL CASE

In this novel approach, we treat both solutes, simple salt and macrosalt (ms) as solutes in their own right. At the cmm, the micellar equilibrium is written as follows.



Then at equilibrium,

$$N \cdot \mu^{\text{eq}}[\{v_+AM^{z+} v_-X^{z-}\} (\text{aq})] = \mu^{\text{eq}}[\{N \cdot v_+AM^{z+}(N-\beta) \cdot v_-X^{z-}\} |\beta^{v(-) \cdot z(-)}| |\beta \cdot v_-| X^{z-}\} (\text{aq})] \quad (21-2)$$

For the macrosalt,

$$\gamma_{\pm}(\text{ms})^{(1+|\beta \cdot v(-)|)} = \gamma_+ \cdot \gamma_-^{|\beta \cdot v(-)|} \quad (21-3)$$

and

$$Q(\text{ms})^{(1+|\beta \cdot v_{-}|)} = 1^{|\beta \cdot v_{-}|} |\beta \cdot v_{-}|^{|\beta \cdot v_{-}|} \quad (21-4)$$

At the cmm,

$$\begin{aligned} \mu(\text{ms}; \text{aq}) &= \mu^0(\text{ms}; \text{aq}) \\ &+ (1 + |\beta \cdot v_{-}|) \cdot R \cdot T \cdot \ln[Q \cdot m(\text{ms}) \cdot \gamma_{\pm}(\text{ms})/m^0] \end{aligned} \quad (21-5)$$

or

$$\begin{aligned} \mu(\text{ms}; \text{aq}) &= \mu^0(\text{ms}; \text{aq}) + [1 + |\beta \cdot v_{-}|] \cdot R \cdot T \cdot \ln Q \\ &+ [1 + |\beta \cdot v_{-}|] \cdot R \cdot T \cdot \ln[m(\text{ms}) \cdot \gamma_{\pm}(\text{ms})/m^0] \end{aligned}$$

or

$$\begin{aligned} \mu(\text{ms}; \text{aq}) &= \mu^0(\text{ms}; \text{aq}) \\ &+ [(1 + |\beta \cdot v_{-}|)/(1 + |\beta \cdot v_{-}|)] \cdot |\beta \cdot v_{-}| \cdot R \cdot T \cdot \ln(|\beta \cdot v_{-}|) \\ &+ R \cdot T \cdot (1 + |\beta \cdot v_{-}|) \ln[m(\text{ms}) \cdot \gamma_{\pm}(\text{ms})/m^0] \end{aligned} \quad (21-6)$$

Then

$$\begin{aligned} \mu(\text{ms}; \text{aq}) &= \mu^0(\text{ms}; \text{aq}) + |\beta \cdot v_{-}| \cdot R \cdot T \cdot \ln(|\beta \cdot v_{-}|) \\ &+ R \cdot T \cdot (1 + |\beta \cdot v_{-}|) \ln[m(\text{ms}) \cdot \gamma_{\pm}(\text{ms})/m^0] \end{aligned} \quad (21-7)$$

Hence,

$$\Delta_{\text{mic}} G^0/R \cdot T = \mu^0(\text{ms}; \text{aq}) - N \cdot \mu^0(\text{salt}; \text{aq}) \quad (21-8)$$

Using Eq. (21-5)

$$\begin{aligned} \Delta_{\text{mic}} G^0/R \cdot T &= N \cdot v(\text{salt}) \cdot \ln[Q(\text{salt}) \cdot \text{cmm} \cdot \gamma_{\pm}(\text{salt})/m^0] \\ &- v(\text{ms}) \cdot \ln[Q(\text{ms}) \cdot m(\text{ms}) \cdot \gamma_{\pm}(\text{ms})/m^0] \end{aligned} \quad (21-9)$$

We adopt the usual procedure and define $\Delta_{\text{mic}} G^0(N)$.

$$\begin{aligned} \Delta_{\text{mic}} G^0(N)/R \cdot T &= v(\text{salt}) \cdot \ln[Q(\text{salt}) \cdot \text{cmm} \cdot \gamma_{\pm}(\text{salt})/m^0] \\ &- (1/N) \cdot v(\text{ms}) \cdot \ln[Q(\text{ms}) \cdot m(\text{ms}) \cdot \gamma_{\pm}(\text{ms})/m^0] \end{aligned} \quad (21-10)$$

If the solutions are ideal and if N is large,

$$\Delta_{\text{mic}}G^0(N)/R \cdot T = v(\text{salt}) \cdot \ln[Q(\text{salt}) \cdot \text{cmm}/m^0] \quad (21-11)$$

Then for a 1:1 salt,

$$\Delta_{\text{mic}}G^0(N) = 2 \cdot R \cdot T \cdot \ln[\text{cmm}/m^0] \quad (21-12)$$

In this analysis the term $\Delta_{\text{mic}}G^0(N)$ refers to the difference in the standard chemical potentials of salt and macrosalt in ideal aqueous solutions where $m(\text{salt}) = m(\text{macrosalt}) = m^0 = 1 \text{ mol kg}^{-1}$. In other words, the standard states are defined satisfactorily. Another formulation uses the explicit formulation for $Q(\text{ms})$.

Then from Eq. (21-9),

$$\Delta_{\text{mic}}G^0/R \cdot T = N \cdot v(\text{salt}) \cdot \ln[Q(\text{salt}) \cdot \text{cmm} \cdot \gamma_{\pm}(\text{salt})/m^0] \\ - |\beta \cdot v_-| \cdot \ln(|\beta \cdot v_-|) - (1 + |\beta \cdot v_-|) \cdot \ln[m(\text{ms}) \cdot \gamma_{\pm}(\text{ms})/m^0] \quad (21-12)$$

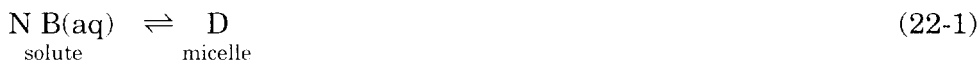
In the limit that no counter ions are bound such that $N = \beta$ and v_- is zero and $Q = 1$, we recover the equation for non-ionic surfactants.

22. DISCUSSION

We commented in Section 1 that our major concern centred on the definition of standard states for salts and micelles. We stressed the point in subsequent sections but then expressed surprise that in nearly all cases the final equations for the standard Gibbs energy of micelle formation are similar. In fact, the similarities increase when this Gibbs energy refers to the change when one mole of monomer is incorporated into the micelle. In the latter case, the procedures which involve dividing all terms in the equation by a large aggregation number produce remarkably similar equations after making a number of apparently reasonable approximations. It is a matter of concern, therefore, how these similarities emerge. We disagree with the view that for large N the phase equilibrium and mass action models become equivalent [34]. Our thesis is that they cannot be equivalent on the grounds that the standard states are dramatically different.

For the purpose of the following discussion, we consider a simple solute $B(\text{aq})$. At a characteristic composition, cmm , these solute molecules aggregate to form micelles D with aggregation number N .

Thus,



At a critical molality the thermodynamic condition for equilibrium is:

$$N \cdot \mu^{\text{eq}}(B; aq) \rightleftharpoons \mu^{\text{eq}}(D; \text{micelles}) \quad (22-2)$$

This equation marks the end of the formal thermodynamics. The next task involves relating the equilibrium chemical potentials to two quantities.

- (I) A standard (reference) chemical potential which we write $\mu^0(j)$ for substance j and which describes either a reference state or a reference composition.
- (II) A composition variable expressing the composition at equilibrium together with an activity coefficient expressing the deviations in the properties of the system from ideal.

In the case of $\mu^{\text{eq}}(B; aq)$, we have used for (I), the reference chemical potential $\mu^0(\text{solute } j; aq; m_j = m^0 = 1 \text{ mol kg}^{-1})$ which we abbreviated to μ_j^0 . For (II), we used the molality cmm and activity coefficient γ_j . Thus for solute j in Eq. (22-2),

$$\begin{aligned} \mu^{\text{eq}}(B; aq) = & \mu^0(B; aq; m_j = 1.0 \text{ mol kg}^{-1}; \text{id}) \\ & + R \cdot T \cdot \ln(\text{cmm} \cdot \gamma_j / m^0) \end{aligned} \quad (22-3)$$

Problems emerge when we attempt the same exercise for micelles, D . In general terms,

$$\begin{aligned} \mu^{\text{eq}}(D\text{-micelles}) = & \mu^0[D; f(\text{micellar reference state})] \\ & + f(\text{micellar composition}) \end{aligned} \quad (22-4)$$

Concentrating attention on the right hand side of Eq. (22-4), how we apportion the contribution of the two terms to $\mu^{\text{eq}}(D\text{-micelles})$ is, in some senses, arbitrary. But if we define *a priori* the contribution from one term that contribution from the other term is defined. What we cannot do is define *a priori* both terms. Unfortunately, this is what happens in the Phase Equilibrium model which develops Eq. (22-4) as follows:

- (I) $\mu^0[D; f(\text{micellar reference state})] = \mu^*(\text{pure micelle})$
- (II) $f(\text{micellar composition}) = \text{zero}$.

By defining *a priori* both terms, there is no guarantee that Eq. (22-4) holds unless these terms float in an arbitrary fashion. If the latter is the case, the analysis loses some of its force.

The Liquid Mixture model develops the argument as follows:

$$(I) \quad \mu^0[D; f(\text{micellar reference state})] = \mu^*(\text{pure micelle})$$

$$(II) \quad f(\text{micellar composition}) = R \cdot T \cdot \ln(x_D \cdot f_D)$$

This approach has merit although the activity coefficient f_D presents problems in that for dilute aqueous solutions f_D is likely to be very different from unity. This difficulty is avoided in the final step by dividing through by the aggregation number. The effect is to remove contribution (II) to $\mu^{\text{eq}}(\text{micelle})$ throwing the whole weight of $\mu^{\text{eq}}(\text{micelle})$ on to term (I), as in the Equilibrium model.

In the Mass Action model terms I and II are defined in the following way:

$$(I) \quad \mu^0[D; f(\text{micellar reference state})] = \mu^0(D; \text{aq}; m_D = 1.0 \text{ mol kg}^{-1}; \text{id})$$

$$(II) \quad f(\text{micellar composition}) = R \cdot T \cdot \ln(m_D \cdot \gamma_D / m^0)$$

Here term I describes a hypothetical ideal solution ($\gamma_D = 1$) solution in which the molality m_D is unity (at the same T and p). We stress that this is a solution reference state. The assumption that in a solution dilute in micelles, γ_D is unity seems acceptable. At this stage the analysis is self consistent. But subsequently in calculating $\Delta_{\text{mic}} G^0(N)$ we lose term II. Then the right hand side of Eq. (22-2) is effectively, $\mu^0(D; \text{aq}; m_D = 1.0 \text{ mol kg}^{-1}; \text{id})$. The similarity between the Mass Action model and the Phase Equilibrium model equations emerges because we have again lost the composition details from the right hand side of Eq. (22-4). Although slightly unsatisfactory the reference state for micelles in the Mass Action model is a solution state, allowing useful comparisons to be drawn with the reference state for the monomers and other solutes. In summary, our prejudice favours the Mass Action model but there is little doubt that these systems offer an interesting thermodynamic challenge.

ACKNOWLEDGEMENTS

We thank SERC for a grant (LGS), the Commonwealth Fellowship Fund (MCSS) and the SERC for the support of the Molecular Recognition Initiative. Also, my long-suffering secretary who lost half of this document through a disk corruption!

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